

Time-dependent current-density functional theory for the friction of ions in an interacting electron gas

V. U. Nazarov

Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan

J. M. Pitarke

CIC nanoGUNE Consolider, Mikeletegi Pasealekua 56, E-2009 Donostia, Basque Country

*Materia Kondentsatuaren Fisika Saila, UPV/EHU and Unidad Fisica de Materiales,
CSIC-UPV/EHU, 644 Posta kutxatila, E-48080 Bilbo, Basque Country*

Y. Takada

Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

G. Vignale

Department of Physics and Astronomy, University of Missouri, Columbia, Missouri 65211, USA

Y.-C. Chang

Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan

Due to the strongly nonlocal nature of $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ the *scalar* exchange and correlation (xc) kernel of the time-dependent density-functional theory (TDDFT), the formula for Q the friction coefficient of an interacting electron gas (EG) for ions tends to give a too large value of Q for heavy ions in the medium- and low-density EG, if we adopt the local-density approximation (LDA) to $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$, even though the formula itself is formally exact. We have rectified this unfavorable feature by reformulating the formula for Q in terms of the *tensorial* xc kernel of the time dependent current-density functional theory, to which the LDA can be applied without intrinsic difficulty. Our numerical results find themselves in a considerably better agreement with the experimental stopping power of Al and Au for slow ions than those previously obtained within the LDA to the TDDFT.

1. Introduction

The problem of the stopping power (SP) of solids for moving ions (the energy-loss by ion per its unit path-length) has been attracting much attention for decades (see, e.g., Ref. ¹ for recent reviews). Theoretically, this problem has been investigated in two distinct ways: One is a perturbation approach in which the projectile-target interaction is taken as an expansion parameter ². The other is based on the density-functional theory (DFT), treating the problem in a fully nonlinear manner from the

outset ^{3; 4}.

For slow projectiles, the perturbation expansion generally fails ⁵, making the nonlinear treatment indispensable. In the limit of zero velocity, the potential scattering (binary-collision) theory is known to give an expression for the friction coefficient (FC) (SP divided by the projectile velocity at its zero value) of electron gas (EG) as ^{6; 3; 4}

$$Q = \bar{n}_0 k_F \sigma_{tr}(k_F), \quad (1)$$

where k_F is the Fermi momentum, $\sigma_{tr}(k_F)$ is the transport cross-section of the elastic scattering of an electron at the Fermi level in the self-consistent Kohn-Sham (KS) ⁷ potential $V_{KS}(r)$ of the ion statically immersed in the EG, and \bar{n}_0 is the density of the homogeneous EG in the absence of the ion. Equation (1) is, however, incomplete ^{8; 9} in the sense that it ignores the role of the *dynamical exchange and correlations* (xc) effects in the problem of the ion slowing. These effects cannot be neglected even at vanishingly small velocities. The complete formal solution to the problem of the friction coefficient of the interacting EG including the dynamical xc effects has been recently found as ¹⁰

$$Q = Q_1 + Q_2, \quad (2)$$

where

$$Q_1 = - \int \frac{[\nabla_{\mathbf{r}} V_{KS}(r) \cdot \mathbf{v}]}{v} \frac{[\nabla_{\mathbf{r}'} V_{KS}(r') \cdot \mathbf{v}]}{v} \times \frac{\partial \text{Im} \chi_{KS}(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \Big|_{\omega=0} d\mathbf{r} d\mathbf{r}', \quad (3)$$

$$Q_2 = - \int \frac{[\nabla_{\mathbf{r}} n_0(r) \cdot \mathbf{v}]}{v} \frac{[\nabla_{\mathbf{r}'} n_0(r') \cdot \mathbf{v}]}{v} \times \frac{\partial \text{Im} f_{xc}(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \Big|_{\omega=0} d\mathbf{r} d\mathbf{r}'. \quad (4)$$

In Eqs. (2)-(4), Q_1 and Q_2 denote, respectively, the independent-electrons and the dynamical xc contributions to the friction coefficient; $\chi_{KS}(\mathbf{r}, \mathbf{r}', \omega)$ and $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ are the KS density-response function and the dynamical xc kernel ¹¹, respectively, of the inhomogeneous many-body system of an ion at rest in the EG, $n_0(r)$ is the ground-state density of this system, and \mathbf{v} is a small velocity of the projectile, on the value of which the final results evidently do not depend.

The dynamical xc kernel is defined as the Fourier transform with respect to time of the functional derivative of the time-dependent xc potential with respect to the time-dependent electron density

$$f_{xc}[n_0(\mathbf{r})](\mathbf{r}, t; \mathbf{r}', t') = \frac{\delta V_{xc}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \Big|_{n=n_0(\mathbf{r})}. \quad (5)$$

A formal proof of Eqs. (2)-(4) is provided in Appendix B.

For the independent-particle contribution, Eq. (3) can be shown to coincide exactly with Eq. (1) of the binary-collision theory (see Appendix D of the present

paper). Actual evaluation of Eq. (1) can be done through a well known procedure⁴ of the self-consistent solution of the KS equations

$$[-(1/2)\Delta + V_{KS}(r)]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}),$$

where $\psi_i(\mathbf{r})$ and ϵ_i are the single-particle wave-functions and the eigenenergies, respectively, in the potential

$$V_{KS}(r) = -Z_1/r + \int [n_0(r') - \bar{n}_0]/|\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + V_{xc}[n_0(r)] - V_{xc}(\bar{n}_0), \quad (6)$$

where Z_1 is the atomic number of the ion, and $V_{xc}[n_0(r)]$ is the xc potential of the static DFT. The ground-state density is determined as

$$n_0(r) = \sum_{\epsilon_i \leq \epsilon_F} |\psi_i(\mathbf{r})|^2, \quad (7)$$

where ϵ_F is the Fermi energy. Upon achievement of self-consistency, the transport cross-section can be conveniently found through¹²

$$\sigma_{tr}(k) = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (l+1) \sin^2[\delta_l(k) - \delta_{l+1}(k)], \quad (8)$$

where $\delta_l(k)$ is the phase-shift of the scattering state with momentum k and angular momentum l .

Determination of both the noninteracting-electron (Q_1) and the dynamical xc (Q_2) parts of the friction coefficient require, respectively, pertinent approximations to the static xc potential $V_{xc}(r)$ and the dynamical xc kernel $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$. The local-density approximation (LDA) provides simple and rather accurate schemes^{13; 14} for the quantities derived from the static xc potential. The situation with the dynamical xc kernel is, however, much more complicated: The scalar xc kernel $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ of the time-dependent density functional theory (TDDFT) is known to be a strongly nonlocal function of space coordinates¹⁵, implying a difficulty in directly constructing an accurate approximation to calculate Q_2 through Eq. (4). On the other hand, it is known¹⁶ that if the current-density rather than the particle-density is chosen as the basic variable of the theory, then the corresponding tensorial xc kernel is a function of short range. This fact made it possible to construct a consistent LDA scheme within the framework of the time-dependent current-density functional theory^{16; 17} (TDCDFT). More recently, the TDCDFT has been successfully applied in studying the damping of excitations in disordered systems¹⁸ and dynamical corrections to the resistance of point contacts¹⁹.

Therefore the main purpose of this paper is to recast Eq. (4) into a form expressed through the tensorial xc kernel of the TDCDFT which allows the LDA treatment. With using this form, we have made comparison between TDDFT and TDCDFT through numerical investigation to find that Q_2 is overestimated in the LDA to the TDDFT for heavy ions immersed in the medium- and low-density EG, while the LDA to the TDCDFT rectifies this unfavorable feature.

It must be noted, that the *exact* TDDFT and the *exact* TDCDFT, were they possible to develop, would yield, of course, exactly the same friction coefficient Q . Both theories would then involve *nonlocal* scalar and tensorial xc kernels, respectively. The basic idea of our method is to express quite generally the scalar xc kernel of TDDFT through the tensorial one of TDCDFT [Eq. (20)]. Then we show that if the local tensorial xc kernel of TDCDFT is used on the right-hand side of this expression, the resulting *nonlocal* scalar xc kernel of TDDFT is free of the inconsistencies of the LDA to TDDFT, and when used in Eq (4), it yields a good description of the many-body dynamical effects in the friction coefficient of the interacting EG for ions.

In Refs. 10; 20 we have summarized main results of the TDDFT and TDCDFT approaches, respectively, to the problem of the stopping power of metals for slow ions. The present work gives rigorous proofs of all the assertions made in Ref. 10; 20 as well as specifies details of both the mathematical formalisms and the computational procedures.

The organization of this paper is as follows: In Sec. 2 and Appendices A - D we present a formal TDDFT of the friction of ions in EG and in Subsection 2.1 we discuss a fundamental difficulty the LDA to the dynamical xc kernel encounters, i.e., the violation within LDA of the requirement that the friction coefficient of free space for isolated atoms and ions must be zero. In Sec. 3 we develop the TDCDFT of the friction of ions in EG and demonstrate the resolution within the LDA to the TDCDFT of the above contradiction (Subsection 3.2 and Appendix E). In Sec. 4 we outline the calculational procedures, present the results and their discussion. Our conclusions are collected in Sec. 5. Appendix F provides explicit expressions for the response functions and xc kernel in the spherical coordinate system that we use in our calculations.

2. Time-dependent density-functional theory of the friction coefficient

We consider a recoilless probe particle of the charge $Z_1 e$, where e is the absolute value of the charge of electron, moving with velocity \mathbf{v} in the otherwise homogeneous gas of interacting electrons at zero temperature. The stopping power is the retarding force that the polarization charge distribution in the vicinity of the projectile exerts on the projectile itself. Accordingly, one can write ² (we use atomic units throughout the paper)

$$-\frac{dE}{dx} = -\frac{Z_1}{v} \int d\mathbf{r} d\mathbf{r}' \delta(\mathbf{r} - \mathbf{v}t) \mathbf{v} \cdot \nabla_{\mathbf{r}} n_{ind}(\mathbf{r}', t) / |\mathbf{r} - \mathbf{r}'|, \quad (9)$$

n_{ind} being the electron density induced by the projectile. Our first step is to obtain the following expression for the friction coefficient of the *interacting* EG:

$$Q \equiv \lim_{v \rightarrow 0} -\frac{1}{v} \frac{dE}{dx} = - \int \frac{[\nabla_{\mathbf{r}} V_0(r) \cdot \mathbf{v}]}{v} \frac{[\nabla_{\mathbf{r}'} V_0(r') \cdot \mathbf{v}]}{v} \frac{\partial \text{Im} \chi(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \Big|_{\omega=0} d\mathbf{r} d\mathbf{r}', \quad (10)$$

where $V_0(r) = -Z_1/r$ is the bare Coulomb potential and $\chi(\mathbf{r}, \mathbf{r}', \omega)$ is the linear density-response function of the system of *interacting* electrons in the static field of an impurity of charge Z_1 at $\mathbf{r} = 0$. A proof of Eq. (10) is provided in Appendix A. We emphasize that Eq. (10) is fully nonlinear with respect to the interaction of the bare charge Z_1 with the EG. The next step, which is performed in Appendix B, is to show that Eq. (10) leads to Eqs. (2) - (4). The equivalence between Eq. (3) and the friction coefficient of Eq. (1) from the binary-collision theory is proven in Appendix D.

2.1. LDA to the TDDFT and the violation of the requirement for the friction coefficient of free space to be zero

Within the LDA, the scalar dynamical xc kernel is given by ¹¹

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc,L}^h[n_0(r), \omega] \delta(\mathbf{r} - \mathbf{r}'), \quad (11)$$

where $f_{xc,L}^h(n, \omega)$ denotes the $q \rightarrow 0$ limit of the frequency-dependent longitudinal xc kernel of a homogeneous EG of the density n . Due to the spherical symmetry of $n_0(r)$, substitution of Eq. (11) into Eq. (4) yields

$$Q_2 = -\frac{4\pi}{3} \int_0^\infty dr [r n_0'(r)]^2 \frac{\partial \text{Im} f_{xc,L}^h[n_0(r), \omega]}{\partial \omega} \Big|_{\omega=0}. \quad (12)$$

An important test of the theory is the limit of zero density of the EG, i.e., $\bar{n}_0 \rightarrow 0$. It is evident that the friction coefficient for any atom (ion) should be zero in this case. The noninteracting-electrons part Q_1 of Eq. (1) obviously satisfies this requirement. However, it is easy to see from Eq. (12) that within the LDA, Q_2 remains finite since the ground-state density $n_0(r)$ of an isolated ion (atom) has a nonzero gradient, and the frequency derivative of $\text{Im} f_{xc,L}^h(n, \omega)$ is always nonzero and negative ²¹. Therefore, the LDA to the scalar xc kernel does not satisfy the requirement of the friction coefficient of vacuum for an atom to be zero.

Let us now demonstrate that the rigorous formula (4) does pass the above test. For an arbitrary bounded (finite) system, which is an atom in vacuum, a sum rule holds ¹⁵

$$\int f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \nabla_{\mathbf{r}'} n_0(\mathbf{r}') d\mathbf{r}' = \nabla_{\mathbf{r}} V_{xc}(\mathbf{r}). \quad (13)$$

Substituting Eq. (13) into Eq. (4) and noting that the right-hand side of the former does not depend on frequency, we obtain zero identically, which proves our assertion.

We note that the sum rule (13) *does not* hold for extended systems and, therefore, Q_2 is finite for atoms (ions) in EG of nonzero density.

Table 1. Inaccuracy of LDA to TDDFT: Friction coefficient of free space ($r_s = \infty$) and that of an electron liquid of $r_s = 2.2$ for several atoms. Line 3 is the ratio of lines 1 and 2 (%).

Atom	He	Be	C	O	Ne	Mg	Si
$Q(r_s = \infty)$	0.04	0.11	0.17	0.24	0.30	0.36	0.43
$Q(r_s=2.2)$	0.34	0.43	0.70	0.46	0.16	0.15	0.54
%	12	25	24	52	188	240	80

To give an idea how large can be the error introduced by LDA to TDDFT, in Table 1 we list the values of FC of free space ($r_s = \infty$) for a number of atoms. For comparison, in column 3 of this table we list the FC of EG of $r_s = 2.2$ for the same atoms obtained with use of Eq. (1) (neglect of dynamical xc).

The shortcoming of the LDA to the TDDFT manifested in the the violation of the requirement of zero friction coefficient of vacuum will be overcome in the next section within the LDA to the TDCDFT.

3. Time dependent current-density functional theory of the friction coefficient

The purpose of this section is to express Eq. (4) for the dynamical xc contribution to the friction coefficient in terms of the xc tensor of the time-dependent TDCDFT in order to overcome the difficulties the LDA encounters when applied to the ordinary TDDFT as discussed in the previous section. We know that ¹⁶

$$\hat{f}_{xc,ij}(\mathbf{r}, \mathbf{r}', \omega) = \hat{\chi}_{KS,ij}^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \hat{\chi}_{ij}^{-1}(\mathbf{r}, \mathbf{r}', \omega) + \frac{c}{\omega^2} \nabla_i \frac{1}{|\mathbf{r} - \mathbf{r}'|} \nabla'_j, \quad (14)$$

where $\hat{f}_{xc,ij}$ is the tensorial xc kernel of the TDCDFT, $\hat{\chi}_{ij}$ is the many-body current density-vector potential response function, and $\hat{\chi}_{KS,ij}$ is the single-particle KS counterpart of the latter. On the other hand, the scalar xc kernel of the ordinary TDDFT can be written as

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \frac{1}{|\mathbf{r} - \mathbf{r}'|}, \quad (15)$$

where χ is the longitudinal density-scalar potential response function and χ_{KS} is its Kohn-Sham counterpart. We can write in operator notations

$$\chi = -\frac{c}{\omega^2} \nabla \cdot \hat{\chi} \cdot \nabla, \quad (16)$$

and consequently

$$\chi^{-1} = -\frac{\omega^2}{c} \nabla^{-2} \nabla \cdot \left(\hat{L} \hat{\chi} \hat{L} \right)^{-1} \cdot \nabla \nabla^{-2}, \quad (17)$$

where \hat{L} is the longitudinal projector operator

$$\hat{L}_{ij} = \nabla_i \nabla_j \nabla^{-2}.$$

Using a simple operator identity

$$\left(\hat{L}\hat{\chi}\hat{L}\right)^{-1} = \hat{L}\hat{\chi}^{-1}\hat{L} - \hat{L}\hat{\chi}^{-1}\left(\hat{T}\hat{\chi}^{-1}\hat{T}\right)^{-1}\hat{\chi}^{-1}\hat{L}, \quad (18)$$

where $\hat{T} = \hat{1} - \hat{L}$ is the transverse projector, we can write for the inverse scalar response function

$$\chi^{-1} = -\frac{\omega^2}{c} \nabla^{-2} \nabla \cdot \left[\hat{\chi}^{-1} - \hat{\chi}^{-1} \left(\hat{T} \hat{\chi}^{-1} \hat{T} \right)^{-1} \hat{\chi}^{-1} \right] \cdot \nabla \nabla^{-2}. \quad (19)$$

Then by Eq. (15) we have

$$f_{xc} = -\frac{\omega^2}{c} \nabla^{-2} \nabla \cdot \left\{ \hat{f}_{xc} + \left(\hat{\chi}_{KS}^{-1} - \hat{f}_{xc} \right) \times \right. \\ \left. \left[\hat{T} \left(\hat{\chi}_{KS}^{-1} - \hat{f}_{xc} \right) \hat{T} \right]^{-1} \left(\hat{\chi}_{KS}^{-1} - \hat{f}_{xc} \right) - \hat{\chi}_{KS}^{-1} \left(\hat{T} \hat{\chi}_{KS}^{-1} \hat{T} \right)^{-1} \hat{\chi}_{KS}^{-1} \right\} \cdot \nabla \nabla^{-2}. \quad (20)$$

Equation (20) constitutes a formal expression for the scalar xc kernel f_{xc} of the ordinary TDDFT in terms of the tensorial xc kernel \hat{f}_{xc} of the TDCDFT and the independent-particle (KS) tensorial response function $\hat{\chi}_{KS}$. Then by virtue of Eqs. (20), (4), (14), and (18) one can write

$$Q_2 = -\frac{1}{c v^2} \lim_{\omega \rightarrow 0} \omega \operatorname{Im} (n_0 - \bar{n}_0) \mathbf{v} \cdot \hat{L} \left\{ \hat{f}_{xc} + \left(\hat{\chi}_{KS}^{-1} - \hat{f}_{xc} \right) \left[\hat{T} \left(\hat{\chi}_{KS}^{-1} - \hat{f}_{xc} \right) \hat{T} \right]^{-1} \right. \\ \left. \times \left(\hat{\chi}_{KS}^{-1} - \hat{f}_{xc} \right) - \hat{\chi}_{KS}^{-1} \left(\hat{T} \hat{\chi}_{KS}^{-1} \hat{T} \right)^{-1} \hat{\chi}_{KS}^{-1} \right\} \hat{L} (n_0 - \bar{n}_0) \mathbf{v}.$$

In the above equation, the operator in the braces is longitudinal from both sides, the fact of which can be verified by applying the \hat{T} operator from either side yielding zero identically. We therefore can drop \hat{L} operators to the result

$$Q_2 = -\frac{1}{c v^2} \lim_{\omega \rightarrow 0} \omega \operatorname{Im} (n_0 - \bar{n}_0) \mathbf{v} \cdot \left\{ \hat{f}_{xc} + \left(\hat{\chi}_{KS}^{-1} - \hat{f}_{xc} \right) \left[\hat{T} \left(\hat{\chi}_{KS}^{-1} - \hat{f}_{xc} \right) \hat{T} \right]^{-1} \right. \\ \left. \times \left(\hat{\chi}_{KS}^{-1} - \hat{f}_{xc} \right) - \hat{\chi}_{KS}^{-1} \left(\hat{T} \hat{\chi}_{KS}^{-1} \hat{T} \right)^{-1} \hat{\chi}_{KS}^{-1} \right\} \cdot (n_0 - \bar{n}_0) \mathbf{v}. \quad (21)$$

Equation (21) is a formal expression for the dynamical part of the friction coefficient in terms of the TDCDFT quantities. It, however, is not easy to use in calculations. We, therefore, proceed to derive an equation which will be shown in Sec. 4 convenient to implement in practical calculations. First, we introduce the notations

$$\mathbf{x} = \left(\hat{T} \hat{\chi}_{KS}^{-1} \hat{T} \right)^{-1} \hat{\chi}_{KS}^{-1} \cdot (n_0 - \bar{n}_0) \mathbf{v}, \quad (22)$$

$$\mathbf{y} = \left(\hat{T} \hat{\chi}^{-1} \hat{T} \right)^{-1} \hat{\chi}^{-1} \cdot (n_0 - \bar{n}_0) \mathbf{v}. \quad (23)$$

Then this is straightforward to show that \mathbf{y} satisfies the equation

$$\mathbf{y} = \mathbf{x} + \left(\hat{T} \hat{\chi}_{KS}^{-1} \hat{T} \right)^{-1} \hat{f}_{xc} \cdot [\mathbf{y} - (n_0 - \bar{n}_0) \mathbf{v}]. \quad (24)$$

Finally, with use of Eq. (24), Eq. (21) can be rewritten as

$$Q_2 = -\frac{1}{c v^2} \lim_{\omega \rightarrow 0} \omega \operatorname{Im} [\mathbf{x} - (n_0 - \bar{n}_0) \mathbf{v}] \cdot \hat{f}_{xc} \cdot [\mathbf{y} - (n_0 - \bar{n}_0) \mathbf{v}]. \quad (25)$$

3.1. The Local Density Approximation for the tensorial xc kernel

Within the LDA to the TDCDFT one can write¹⁷

$$\begin{aligned} \int f_{xc,ij}(\mathbf{r}, \mathbf{r}', \omega) s_j(\mathbf{r}') d\mathbf{r}' &= \frac{ic}{\omega} \times \\ &\left[-\nabla_i V_{xc}^{ALDA}(\mathbf{r}, \omega) + \frac{1}{n_0(\mathbf{r})} \nabla_j \sigma_{xc,ij}(\mathbf{r}, \omega) \right], \end{aligned} \quad (26)$$

where

$$V_{xc}^{ALDA}(\mathbf{r}, \omega) = \frac{1}{i\omega} \epsilon''_{xc}[n_0(\mathbf{r})] \nabla_j s_j(\mathbf{r}), \quad (27)$$

$\epsilon_{xc}(n)$ is the xc energy density of the homogeneous EG of density n ,

$$\begin{aligned} \sigma_{xc,ij}(\mathbf{r}, \omega) &= \tilde{\eta}_{xc}[n_0(\mathbf{r}), \omega] [\nabla_j u_i(\mathbf{r}) + \nabla_i u_j(\mathbf{r}) \\ &- \frac{2}{3} \nabla_k u_k(\mathbf{r}) \delta_{ij}] + \tilde{\zeta}_{xc}[n_0(\mathbf{r}), \omega] \nabla_k u_k(\mathbf{r}) \delta_{ij}, \end{aligned} \quad (28)$$

where

$$\mathbf{u}(\mathbf{r}) = \mathbf{s}(\mathbf{r})/n_0(\mathbf{r}),$$

the viscosity coefficients are given by

$$\begin{aligned} \tilde{\zeta}_{xc}(n, \omega) &= -\frac{n^2}{i\omega} \left[f_{xc,L}^h(n, \omega) - \frac{4}{3} f_{xc,T}^h(n, \omega) - \epsilon''_{xc}(n) \right], \\ \tilde{\eta}_{xc}(n, \omega) &= -\frac{n^2}{i\omega} f_{xc,T}^h(n, \omega), \end{aligned} \quad (29)$$

and $f_{xc,L}^h(n, \omega)$ and $f_{xc,T}^h(n, \omega)$ are, respectively, the longitudinal and transverse xc kernels of the homogeneous EG with the density n .

3.2. Resolution within the TDCDFT of the problem of the finite friction coefficient of vacuum

To show that within the LDA to the TDCDFT the friction coefficient of vacuum is zero, it is sufficient to prove that with the tensorial xc kernel of the previous subsection and the scalar xc kernel obtained from it by Eq. (20), the sum rule of

Eq. (13) holds. We proceed by recalling exact sum rules for the tensorial quantities²²

$$\int \hat{f}_{xc,ij}(\mathbf{r}, \mathbf{r}', \omega) n_0(\mathbf{r}') d\mathbf{r}' = -\frac{c}{\omega^2} \nabla_i \nabla_j V_{xc}(\mathbf{r}), \quad (30)$$

$$\frac{c}{\omega^2} \int \hat{\chi}_{KS,ik}(\mathbf{r}, \mathbf{r}', \omega) \nabla'_k \nabla'_j V_{KS}(\mathbf{r}') d\mathbf{r}' = c \int \hat{\chi}_{KS,ij}(\mathbf{r}, \mathbf{r}', \omega) d\mathbf{r}' - n_0(\mathbf{r}) \delta_{ij} \quad (31)$$

$$\frac{c}{\omega^2} \int \hat{\chi}_{ik}(\mathbf{r}, \mathbf{r}', \omega) \nabla'_k \nabla'_j V_0(\mathbf{r}') d\mathbf{r}' = c \int \hat{\chi}_{ij}(\mathbf{r}, \mathbf{r}', \omega) d\mathbf{r}' - n_0(\mathbf{r}) \delta_{ij}, \quad (32)$$

where $V_{xc}(\mathbf{r})$ is the static xc potential. With the LDA to \hat{f}_{xc} of the previous section, the sum rules (30) - (32) are satisfied by construction²². In Appendix E we prove that *for a finite system* the tensorial sum rules (30) - (32) entail the scalar sum rule (13). As soon as the latter is satisfied, results of Sec. 2.1 lead to the zero friction coefficient of vacuum within the LDA to the TDCDFT.

4. Computational procedures, results, and discussion

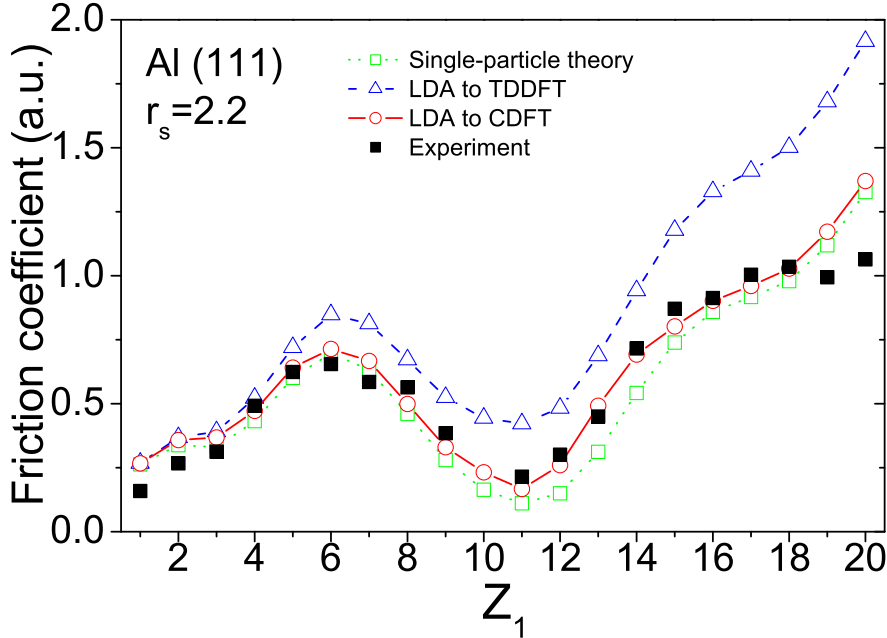


Fig. 1. Friction coefficient of a homogeneous EG of $r_s = 2.2$ versus the projectile charge Z_1 . The open squares are the results of the calculation with neglect of the dynamical xc as obtained from Eq. (1). Triangles are the results of the calculation with the dynamical xc included within the LDA to the conventional TDDFT as obtained from Eq. (12). Open circles are the results of the calculation with the dynamical xc included within the LDA to the TDCDFT as described in Sec. 4. Solid squares are the measured SP of Al of Ref.²³ for slow ions ($v = 0.5$ a.u.) moving at a distance of 1.2 a.u. from the last atomic plane of the Al (111) surface.

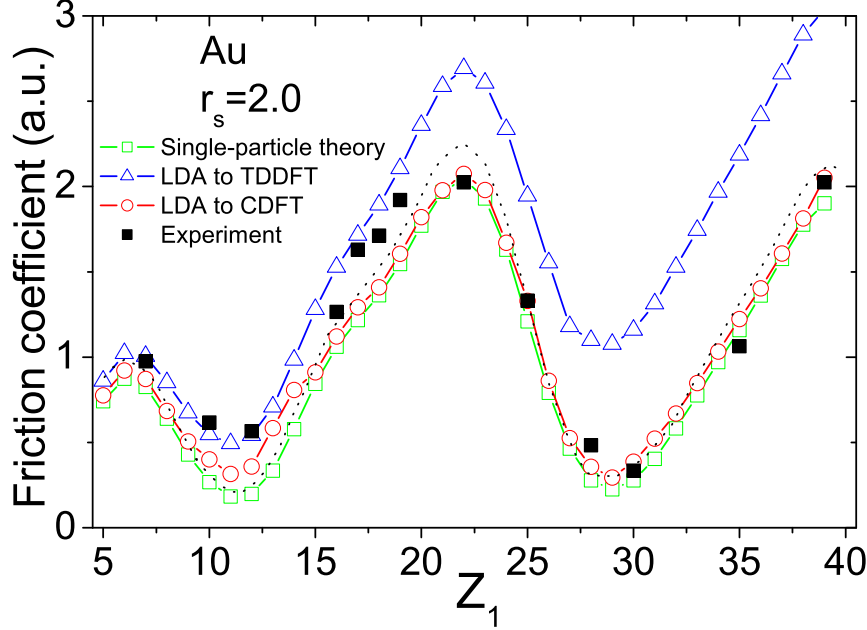


Fig. 2. Friction coefficient of a homogeneous EG of $r_s = 2$ versus the projectile charge Z_1 . Open squares are the results of the calculation with neglect of the dynamical xc as obtained from Eq. (1). Triangles are the results of the calculation with the dynamical xc included within the LDA to the conventional TDDFT as obtained from Eq. (12). Open circles are the results of the calculation with the dynamical xc included within the LDA to the TDCDFT as described in Sec. 4. Solid squares are the measurements of Ref. ²⁴ of the SP of Au for slow ions ($v = 0.68$ a.u.) channeled along the (110) direction. The dotted line is the calculation of Ref. ⁸ with the dynamical xc effects included in the framework of the linear-response theory.

We solve Eq. (24) for the \mathbf{y} vector at finite frequencies, then substitute the results into Eq. (25). The friction coefficient is found by the extrapolation from finite to zero frequency. To conveniently treat $(\hat{T}\hat{\chi}_{KS}^{-1}\hat{T})^{-1}$ in the right-hand side of Eq. (24), we use the identity

$$(\hat{T}\hat{\chi}_{KS}^{-1}\hat{T})^{-1} = \hat{\chi}_{KS} + \frac{c}{\omega^2} \hat{\chi}_{KS} \cdot \nabla \chi_{KS}^{-1} \nabla \cdot \hat{\chi}_{KS}, \quad (33)$$

and equations (F.2)-(F.5) and (F.7) - (F.8) are utilized for the explicit evaluation of the $\hat{\chi}_{KS}$ and \hat{f}_{xc} operators, respectively. With these provisions, the numerical procedure is to approximate Eq. (24) by using a complete ortho-normal set of basis functions thus reducing the problem to a system of linear equations. The natural choice for the radial basis functions is

$$\phi_n(r) = [\alpha^3(n+1)(n+2)]^{-1/2} e^{-r/(2\alpha)} L_n^{(2)}(r/\alpha), \quad (34)$$

where $L_n^{(k)}(x)$ are the associated Laguerre polynomials ^a, and α is a scaling param-

^a $k = 2$ ensures the orthonormality of the radial basis functions with the weight of r^2 .

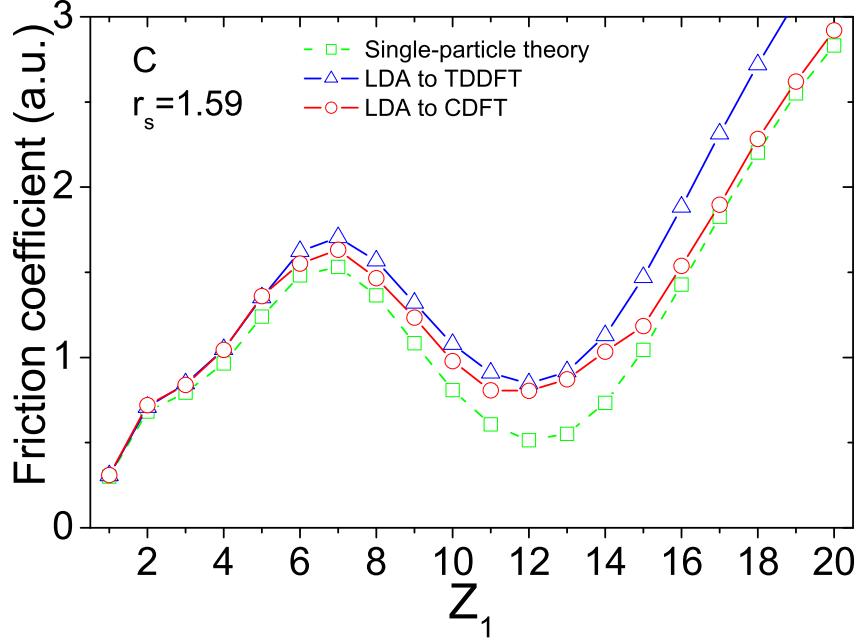


Fig. 3. Friction coefficient of a homogeneous EG of carbon density ($r_s = 1.59$) versus the projectile charge Z_1 . Open squares are the results of the calculation with neglect of the dynamical xc as obtained from Eq. (1). Open triangles are the results of the calculation with the dynamical xc included within the LDA to the conventional TDDFT as obtained from Eq. (12). Open circles are the results of the calculation with the dynamical xc included within the LDA to the TDCDFT as described in Sec. 4. Solid circles, triangles, and diamonds are transmission measurements from Refs. 25, 26, and 27 of the random SP of C for ions moving with velocities $v = 0.41, 0.83$, and 0.25 a.u., respectively.

eter. Since the exact results should not depend on the choice of the basis functions, we have been checking the convergence of the numerical procedure by varying α and making sure that the respective results differ insignificantly.

In Fig. 1, we plot the friction coefficient of EG of $r_s = 2.2$ versus the atomic number of a moving ion. Results of the calculations with neglect of the dynamical xc [the binary-collisions approximation, Eq. (1)], the LDA to TDDFT [the sum of Eq. (1) and Eq. (12)], and the LDA to TDCDFT [the sum of Eq. (1) and Eq. (25)] are shown together with the experimental data of Ref. 23 for ions moving with the velocity of 0.5 a.u. at the distance of 1.2 a.u. from the last atomic plane of the (111) surface of aluminum. The inhomogeneity of the electron density the ions travel through is not strong under these conditions, and in the calculations we have used r_s estimated experimentally 23. Moreover, the experimental SP is predominantly electronic since the trajectory of the projectile ion remains well separated from the lattice atoms. Together, these two conditions justify the comparison with the theory within the homogeneous EG model. The non-monotonic dependence of the friction coefficient on the atomic number of the projectile (the so-called Z_1 -oscillations) is

known to result within the single-particle theory from the competition between the increase in the EG-ion interaction with the growing charge of the bare nucleus of the ion and the decrease of the same interaction due to the screening by the formation of shells of bounded electrons of the pseudo-atom as well as its resonant states, as discussed in detail in Ref. ⁴.

While the LDA to the conventional TDDFT (triangles in Fig. 1) largely overestimates the friction coefficient at $Z_1 \geq 5$, the LDA to the TDCDFT (open circles in Fig. 1) is in a good agreement with the experiment in a wide range of $3 \leq Z_1 \leq 18$. The significant deviation of our results from the experiment occurs at $Z_1 = 1, 2, 19, 20$, where the experimental friction coefficient is *lower* than the binary-collisions calculations (open circles in Fig. 1). This feature has been recently shown to be a single-particle effect due to the finite velocity of the projectiles ²⁸, hence it is an effect of the deviation from the linear dependence of the SP on the velocity. The same effect gives *positive* contribution at $8 \leq Z_1 \leq 12$ suggesting that combined with the many-body effects of the present theory the agreement with the experiment can be further improved. ^b In the range $13 \leq Z_1 \leq 17$, the dynamical many-body effects seem to be solely responsible for the enhancement of the friction coefficient compared with the binary-collisions calculation results.

In Fig. 2, we plot the friction coefficient of EG of $r_s = 2$ versus the atomic number of ions in the range $5 \leq Z_1 \leq 39$. This is compared with the available measured SP for ions with the velocity of 0.68 a.u. channeled along the (110) direction in gold. Now because of the channeling, the collisions with the lattice atoms again do not give significant contribution to the SP. We can see that the general trend is that the LDA to TDCDFT improves the agreement between the theory and the experiment. However, within the range $16 \leq Z_1 \leq 19$ the dynamical xc contribution is too small to account for the onset at the experimental data, nor can the persistent enhancement of the friction coefficient in this range be attributed to the finite velocity effects within the single-particles theory ²⁸. Further studies are required to elucidate the nature of this onset, one of the possible causes being evidently the band-structure effects.

In Fig. 3, we plot the results for EG of $r_s = 1.59$ corresponding to the valence electron-density of carbon. It is instructive to note that within the range $1 \leq Z_1 \leq 14$ the results within the LDA to the TDCDFT and the LDA to the TDDFT do not differ significantly, which can be believed to be true in the general case for light atoms in the high-density EG. Then at higher Z_1 rather abruptly the dynamical

^bThere is no reason, of course, for these two effects to be additive. It must be noted, that Ref. ²⁸ incorrectly attributes the overestimation by Ref. ¹⁰ of the contribution of the many-body effects to the use of the *total* ground-state density rather than the density of the delocalized states only. The total particle-density is, however, the basic variable of the TDDFT and without any artificial assumptions it enters the rigorous result of Eq. (4). The real source of the overestimation of the dynamical xc effects in Ref. ¹⁰ was, as Ref. ¹⁰ had anticipated and the present work shows, use of the LDA within the conventional TDDFT. The present work is overcoming this shortcoming within the LDA to the TDCDFT.

xc contribution almost vanishes, which effect also can be understood qualitatively recalling that for heavy atoms immersed in EG the charge-density distribution (the main quantity entering the theory within the LDA to the TDCDFT) is close to that of isolated atoms, and hence according to the results of Sec. 3.2 it should disappear. The experimental data in Fig. 3 correspond to the SP for ions moving along random trajectories inside bulk carbon and, therefore, they are strongly influenced by the collisions with lattice atoms, which fact hinders the quantitative comparison with the calculations within the EG model.

It must be noted that the LDA to TDCDFT has no strict justification in the $\omega \rightarrow 0$ limit.¹⁶ Nevertheless, the calculations of the *static* polarizabilities of conjugated polymers using the Vignale-Kohn functional in the form of Eqs. (27)-(29) have proved to be very successful.^{29; 30} In this respect, the situation seems to be analogous to that with the LDA to static DFT, which had been justified for weakly varying electron densities only, while the range of its successful applications has proved to be incomparably broader. Similar to the method of Refs.^{29; 30}, we have been performing our calculations at finite ω then extrapolating to $\omega = 0$.

5. Conclusions

Within the current-density functional theory, we have derived equations for the dynamical contribution to the friction coefficient for ions moving in electron gas. The resulting theory demonstrates a crucial advantage over the ordinary time-dependent density-functional approach since within the local-density approximation the former ensures the correct zero friction coefficient in the limit of zero density of the electron gas, while the latter does not.

We have traced the breakdown of the LDA to the ordinary TDDFT to the violation of a previously known sum rule for the scalar exchange and correlation kernel.

Finally, we have performed calculations within the framework of the new theory with the results finding themselves in a good overall agreement with the experimental electronic stopping power of (i) the near-surface region of aluminum for slow ions moving in the grazing geometry and (ii) gold for slow ions moving under a channeling condition.

Appendix A. Proof of Eq. (10)

For a projectile moving in a homogeneous medium, we can rewrite Eq. (9) in the reciprocal space as

$$-\frac{dE}{dx} = (2\pi)^3 \text{Im} \int \frac{\mathbf{v} \cdot \mathbf{q}}{v} v_q n_{ind}(q) dq,$$

where $q = (\mathbf{q}, \omega)$ and

$$v_q = \frac{Z_1}{2\pi^2 \mathbf{q}^2}.$$

An external potential $\phi_{ext}(q)$ induces in the homogeneous EG the particle density

$$n_{ind}(q) = \sum_{n=1}^{\infty} \int dq_1 \dots dq_{n-1} \chi_n(q, q_1, \dots, q_{n-1}) \phi_{ext}(q - q_1) \\ \times \phi_{ext}(q_1 - q_2) \dots \phi_{ext}(q_{n-2} - q_{n-1}) \phi_{ext}(q_{n-1}),$$

where $\chi_n(q, q_1, \dots, q_{n-1})$ is the n -fold many-body density-response function of the homogeneous EG which satisfies $n - 1$ symmetry relations

$$\chi_n(q_0, \dots, q_j, q_{j+1}, \dots, q_{n-1}) = \\ \chi_n(q_0, \dots, q_j, q_j - q_{n-1}, \dots, q_j - q_{j+1}), \quad 0 \leq j < n - 1. \quad (\text{A.1})$$

Since the bare potential by the projectile is

$$\phi_{ext}(q) = v_q \delta(\omega - \mathbf{v} \cdot \mathbf{q}),$$

we can write

$$n_{ind}(q) = \delta(\omega - \mathbf{v} \cdot \mathbf{q}) \sum_{n=1}^{\infty} \int \chi_n(q, q_1, \dots, q_{n-1}) \\ \times v_{q_{n-1}} v_{q_{n-2} - q_{n-1}} \dots v_{q - q_1} d\mathbf{q}_1 \dots d\mathbf{q}_{n-1},$$

where now $q = (\mathbf{q}, \mathbf{v} \cdot \mathbf{q})$. Then we can write for the stopping power

$$- \frac{dE}{dx} = (2\pi)^3 \text{Im} \sum_{n=1}^{\infty} \int \frac{\mathbf{v} \cdot \mathbf{q}_0}{v} \\ \times f_n(q, q_1, \dots, q_{n-1}) d\mathbf{q}_0 \dots d\mathbf{q}_{n-1}, \quad (\text{A.2})$$

where we have introduced the notation

$$f_n(q_0, q_1, \dots, q_{n-1}) = \chi_n(q_0, q_1, \dots, q_{n-1}) \\ \times v_{q_{n-1}} v_{q_{n-2} - q_{n-1}} \dots v_{q_0 - q_1} v_{q_0}. \quad (\text{A.3})$$

For the friction coefficient, which is the stopping power divided by the projectile velocity at its zero value, we can write

$$Q = (2\pi)^3 \text{Im} \sum_{n=1}^{\infty} \sum_{j=0}^{n-1} \int \frac{(\mathbf{v} \cdot \mathbf{q}_0)}{v} \frac{(\mathbf{v} \cdot \mathbf{q}_j)}{v} \\ \times f_{nj}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) d\mathbf{q}_0 \dots d\mathbf{q}_{n-1}, \quad (\text{A.4})$$

where we have introduced further notations

$$f_{nj}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) = \left. \frac{\partial f_n(q_0, \dots, q_{n-1})}{\partial \omega_j} \right|_{\omega_0=0, \dots, \omega_{n-1}=0}.$$

Our purpose is to prove that

$$Q = P, \quad (\text{A.5})$$

where

$$P = (2\pi)^3 \text{Im} \int d\mathbf{q} d\mathbf{k} \frac{(\mathbf{q} \cdot \mathbf{v})}{v} \frac{(\mathbf{k} \cdot \mathbf{v})}{v} v_q v_k \times \frac{\partial \chi(\mathbf{q}, \mathbf{k}, \omega)}{\partial \omega} \Big|_{\omega=0}, \quad (\text{A.6})$$

and $\chi(\mathbf{q}, \mathbf{k}, \omega)$ is the linear density-response function of the system of the charge Z_1 at rest in the EG at origin. The density induced in a homogeneous EG by a wave-vector and frequency dependent external perturbation $\psi_{ext}(\mathbf{q}, \omega)$ plus the static potential of the charge is

$$n_{ind}(q) = \sum_{n=1}^{\infty} \int dq_1 \dots dq_{n-1} \chi_n(q, q_1, \dots, q_{n-1}) \times \phi_{ext}(q - q_1) \dots \phi_{ext}(q_{n-2} - q_{n-1}) \phi_{ext}(q_{n-1}), \quad (\text{A.7})$$

$$\phi_{ext}(q) = \psi_{ext}(q) + v_q \delta(\omega). \quad (\text{A.8})$$

Hence, to express the linear response function of the combined system of the EG with the charge Z_1 at the origin, we must collect in Eq. (A.7) terms linear in $\psi_{ext}(q)$. With the use of symmetries (A.1), we readily arrive at the result

$$\begin{aligned} \chi(\mathbf{q}, \mathbf{k}, \omega) &= \chi_1(\mathbf{q}, \omega) \delta(\mathbf{q} - \mathbf{k}) + 2v_{q-k} \chi_2(\mathbf{q}, \omega, \mathbf{k}, \omega) \\ &+ \sum_{n=3}^{\infty} n \int \chi_n(\mathbf{q}, \omega, \mathbf{q}_1, \omega, \dots, \mathbf{q}_{n-2}, \omega, \mathbf{k}, \omega) \\ &\times v_{q-q_1} \dots v_{q_{n-2}-k} d\mathbf{q}_1 \dots d\mathbf{q}_{n-2}, \end{aligned}$$

where the dependence on the wave-vectors and frequencies has been written explicitly. Hence, by virtue of Eq. (A.6)

$$P = (2\pi)^3 \text{Im} \sum_{n=1}^{\infty} n \int \frac{(\mathbf{q}_0 \cdot \mathbf{v})}{v} \frac{(\mathbf{q}_{n-1} \cdot \mathbf{v})}{v} \times \frac{\partial}{\partial \omega} f_n(\mathbf{q}_0, \omega, \dots, \mathbf{q}_{n-1}, \omega) d\mathbf{q}_0 \dots d\mathbf{q}_{n-1} \Big|_{\omega=0},$$

or

$$P = (2\pi)^3 \text{Im} \sum_{n=1}^{\infty} n \sum_{j=0}^{n-1} \int \frac{(\mathbf{q}_0 \cdot \mathbf{v})}{v} \frac{(\mathbf{q}_{n-1} \cdot \mathbf{v})}{v} \times f_{nj}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) d\mathbf{q}_0 \dots d\mathbf{q}_{n-1}.$$

From Eqs. (A.1) and (A.3) it follows that f_n functions satisfy the same symmetry relations as χ_n

$$\begin{aligned} f_n(q_0, \dots, q_j, q_{j+1}, \dots, q_{n-1}) &= \\ f_n(q_0, \dots, q_j, q_j - q_{n-1}, \dots, q_j - q_{j+1}), 0 \leq j < n-1. \end{aligned} \quad (\text{A.9})$$

A.1.

For brevity, throughout the derivations below by $\int \dots$ we imply the integral $\int d\mathbf{q}_1 \dots d\mathbf{q}_{n-1} \dots$. By Eq. (A.9), for $j < i$ we can write

$$\begin{aligned} \int \mathbf{q}_j f_{ni}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) &= - \int \mathbf{q}_j f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{i-1}, \mathbf{q}_{i-1} - \mathbf{q}_{n-1}, \dots, \mathbf{q}_{i-1} - \mathbf{q}_i) = \\ &- \int \mathbf{q}_j f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{i-1}, \mathbf{q}_{n-1}, \dots, \mathbf{q}_{i+1}, \mathbf{q}_i) = - \int \mathbf{q}_j f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}), \end{aligned} \quad (\text{A.10})$$

where we have used the integration variables $\mathbf{q}_i, \dots, \mathbf{q}_{n-1}$ substitutions leaving other variables intact. But for $j < n-1$

$$\begin{aligned} \int \mathbf{q}_j f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) &= - \int \mathbf{q}_j f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{n-2}, \mathbf{q}_{n-2} - \mathbf{q}_{n-1}) \\ &= - \int \mathbf{q}_j f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}), \end{aligned} \quad (\text{A.11})$$

which shows that for $j < n-1$

$$\int \mathbf{q}_j f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) = 0, \quad (\text{A.12})$$

and then by Eq. (A.10)

$$\int \mathbf{q}_j f_{ni}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) = 0, \quad j < i. \quad (\text{A.13})$$

Further, if $0 < j \leq i \leq n-1$, we can write

$$\begin{aligned} \int \mathbf{q}_i f_{nj}(\mathbf{q}_0, \dots, \mathbf{q}_k, \mathbf{q}_{k+1}, \dots, \mathbf{q}_{n-1}) &= - \int \mathbf{q}_i f_{n,n+k-j}(\mathbf{q}_0, \dots, \mathbf{q}_k, \mathbf{q}_k - \mathbf{q}_{n-1}, \dots, \mathbf{q}_k - \mathbf{q}_{k+1}) = \\ &= \int (\mathbf{q}_i - \mathbf{q}_k) f_{n,n+k-j}(\mathbf{q}_0, \dots, \mathbf{q}_k, \mathbf{q}_{n-1}, \dots, \mathbf{q}_{k+1}) = \int (\mathbf{q}_{n+k-i} - \mathbf{q}_k) f_{n,n+k-j}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}). \end{aligned}$$

The first term in the last expression disappears due to Eq. (A.13), and we have

$$\int \mathbf{q}_i f_{nj}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) = \int \mathbf{q}_{n+k-i} f_{n,n+k-j}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}). \quad (\text{A.14})$$

If $i > j$, then $n+k-i < n+k-j$, and using Eq. (A.13) again we have

$$\int \mathbf{q}_j f_{ni}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) d\mathbf{q}_0 \dots d\mathbf{q}_{n-1} = 0, \quad i \neq 0, j \neq i. \quad (\text{A.15})$$

Putting $i = j$ and $k = j-1$ in Eq. (A.14), we obtain

$$\int \mathbf{q}_j f_{nj}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) = \int \mathbf{q}_{n-1} f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}), \quad j \neq 0. \quad (\text{A.16})$$

A.2.

For $0 < j \leq n-1$ we can write

$$\begin{aligned} \int \sum_{s=j}^{n-1} \mathbf{q}_s f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) &= \int \sum_{s=j}^{n-1} \mathbf{q}_s f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{j-1}, \mathbf{q}_{j-1} - \mathbf{q}_{n-1}, \dots, \mathbf{q}_{j-1} - \mathbf{q}_j) = \\ \int [(n-j)\mathbf{q}_{j-1} - \sum_{s=j}^{n-1} \mathbf{q}_s] f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{j-1}, \mathbf{q}_{n-1}, \dots, \mathbf{q}_j) &= \int [(n-j)\mathbf{q}_{j-1} - \sum_{s=j}^{n-1} \mathbf{q}_s] f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}). \end{aligned}$$

Then

$$\begin{aligned} 2 \int \sum_{s=j}^{n-1} \mathbf{q}_s f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) d\mathbf{q}_0 \dots d\mathbf{q}_{n-1} &= \\ (n-j) \int \mathbf{q}_{j-1} f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) d\mathbf{q}_0 \dots d\mathbf{q}_{n-1}. \end{aligned} \quad (\text{A.17})$$

Using Eq. (A.17), we prove that

$$\begin{aligned} \int \mathbf{q}_j f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) &= \\ (n-j) \int \mathbf{q}_{n-1} f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}), \quad j > 0 \end{aligned} \quad (\text{A.18})$$

by induction from $j = n-1$ to $j = 1$. For $0 < i \leq n-1$, we can write

$$\begin{aligned} \int \mathbf{q}_i f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) &= \int \mathbf{q}_i \sum_{j=0}^{n-1} f_{nj}(\mathbf{q}_0, \mathbf{q}_0 - \mathbf{q}_{n-1}, \dots, \mathbf{q}_0 - \mathbf{q}_1) = \int (\mathbf{q}_0 - \mathbf{q}_i) \sum_{j=0}^{n-1} f_{nj}(\mathbf{q}_0, \mathbf{q}_{n-1}, \dots, \mathbf{q}_1) = \\ \int (\mathbf{q}_0 - \mathbf{q}_{n-i}) \sum_{j=0}^{n-1} f_{nj}(\mathbf{q}_0, \mathbf{q}_1, \dots, \mathbf{q}_{n-1}) &= \int (\mathbf{q}_0 - \mathbf{q}_{n-i}) f_{n0}(\mathbf{q}_0, \mathbf{q}_1, \dots, \mathbf{q}_{n-1}) - \int \mathbf{q}_{n-i} f_{n,n-i}(\mathbf{q}_0, \mathbf{q}_1, \dots, \mathbf{q}_{n-1}), \end{aligned}$$

and then for $0 < i \leq n-1$

$$\int (\mathbf{q}_i + \mathbf{q}_{n-i} - \mathbf{q}_0) f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) = - \int \mathbf{q}_{n-i} f_{n,n-i}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}). \quad (\text{A.19})$$

With use of Eqs. (A.18) and (A.16), Eq. (A.19) gives

$$\int (n\mathbf{q}_{n-1} - \mathbf{q}_0) f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) = - \int \mathbf{q}_{n-1} f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}). \quad (\text{A.20})$$

A.3.

We write

$$\begin{aligned} P - Q &= \frac{(2\pi)^3}{v^2} \text{Im} \sum_{n=1}^{\infty} \sum_{j=0}^{n-1} \int (\mathbf{q}_0 \cdot \mathbf{v}) [(n\mathbf{q}_{n-1} - \mathbf{q}_j) \cdot \mathbf{v}] f_{nj}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) d\mathbf{q}_0 \dots d\mathbf{q}_{n-1} = \\ \frac{(2\pi)^3}{v^2} \text{Im} \sum_{n=1}^{\infty} \int (\mathbf{q}_0 \cdot \mathbf{v}) &\left\{ [(n\mathbf{q}_{n-1} - \mathbf{q}_0) \cdot \mathbf{v}] f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) + \sum_{j=1}^{n-1} [(n\mathbf{q}_{n-1} - \mathbf{q}_j) \cdot \mathbf{v}] f_{nj}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) \right\} d\mathbf{q}_0 \dots d\mathbf{q}_{n-1} \end{aligned}$$

$$= \frac{(2\pi)^3}{v^2} \text{Im} \sum_{n=1}^{\infty} \int (\mathbf{q}_0 \cdot \mathbf{v}) \{ [(n\mathbf{q}_{n-1} - \mathbf{q}_0) \cdot \mathbf{v}] f_{n0}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) + (\mathbf{q}_{n-1} \cdot \mathbf{v}) f_{n,n-1}(\mathbf{q}_0, \dots, \mathbf{q}_{n-1}) \} d\mathbf{q}_0 \dots d\mathbf{q}_{n-1} = 0,$$

where the second equality is due to Eqs. (A.15) and (A.16) and the fourth equality is due to Eq. (A.20).

Appendix B. Proof of Eqs. (2) - (4)

We can rewrite Eq. (10) in the form

$$Q = \int \frac{[\nabla_{\mathbf{r}} V_0(r) \cdot \mathbf{v}]}{v} \frac{[\nabla_{\mathbf{r}'} V_0(r') \cdot \mathbf{v}]}{v} \chi(\mathbf{r}, \mathbf{r}'', 0) \frac{\partial \text{Im} \chi^{-1}(\mathbf{r}'', \mathbf{r}''', \omega)}{\partial \omega} \Big|_{\omega=0} \chi(\mathbf{r}''', \mathbf{r}', 0) d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''',$$

or with use of the static sum rule (C.1) of the next section

$$Q = \int \frac{[\nabla_{\mathbf{r}} n_0(r) \cdot \mathbf{v}]}{v} \frac{[\nabla_{\mathbf{r}'} n_0(r') \cdot \mathbf{v}]}{v} \frac{\partial \text{Im} \chi^{-1}(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \Big|_{\omega=0} d\mathbf{r} d\mathbf{r}'.$$

Taking use of Eq. (15), we have

$$Q = \int \frac{[\nabla_{\mathbf{r}} n_0(r) \cdot \mathbf{v}]}{v} \frac{[\nabla_{\mathbf{r}'} n_0(r') \cdot \mathbf{v}]}{v} \left[\frac{\partial \text{Im} \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \Big|_{\omega=0} - \frac{\partial \text{Im} f_{xc}(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \Big|_{\omega=0} \right] d\mathbf{r} d\mathbf{r}',$$

or

$$Q = - \int \frac{[\nabla_{\mathbf{r}} n_0(r) \cdot \mathbf{v}]}{v} \frac{[\nabla_{\mathbf{r}'} n_0(r') \cdot \mathbf{v}]}{v} \frac{\partial \text{Im} f_{xc}(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \Big|_{\omega=0} d\mathbf{r} d\mathbf{r}' + \\ - \int \frac{[\nabla_{\mathbf{r}} n_0(r) \cdot \mathbf{v}]}{v} \frac{[\nabla_{\mathbf{r}'} n_0(r') \cdot \mathbf{v}]}{v} \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r}'', 0) \frac{\partial \text{Im} \chi_{KS}(\mathbf{r}'', \mathbf{r}''', \omega)}{\partial \omega} \Big|_{\omega=0} \chi_{KS}^{-1}(\mathbf{r}''', \mathbf{r}', 0) d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}'''.$$

Finally, using the static sum rule (C.2) to simplify the second term, we immediately arrive at Eqs. (2) - (4).

Appendix C. Static sum rules for the scalar response-functions

A static shift of an ion by an infinitesimal vector $\Delta \mathbf{r}$ must result in the same shift of the ground-state electron density. The perturbation corresponding to this shift is

$$\Delta V_0(\mathbf{r}) = \Delta \mathbf{r} \cdot \nabla V_0(r)$$

and the change in the electron particle-density due to this shift is

$$\Delta n_0(\mathbf{r}) = \Delta \mathbf{r} \cdot \nabla n_0(r),$$

which leads us to the static sum-rule

$$\int \chi(\mathbf{r}, \mathbf{r}', 0) \nabla' V_0(r') d\mathbf{r}' = \nabla n_0(r). \quad (\text{C.1})$$

The same sum rule evidently holds for the non-interacting KS density-response function

$$\int \chi_{KS}(\mathbf{r}, \mathbf{r}', 0) \nabla' V_{KS}(r') d\mathbf{r}' = \nabla n_0(r). \quad (\text{C.2})$$

Finally, inverting the above two equations and using Eq. (15), we arrive at the static sum-rule for the scalar xc kernel

$$\int f_{xc}(\mathbf{r}, \mathbf{r}', 0) \nabla' n_0(r') d\mathbf{r}' = \nabla V_{xc}(r).$$

We note, that although the sum rules of this Appendix follow as the static limit from the corresponding dynamical sum rules of Ref. ¹⁵, the former hold for extended systems as well, while the latter are valid for bounded (finite) systems only, fact of which necessitates the independent derivation of this Appendix.

Appendix D. Proof of the equivalence between Eqs. (3) and (1)

The imaginary part of the KS response-function can be written as

$$\begin{aligned} \text{Im } \chi_{KS}(\mathbf{q}, \mathbf{k}, \omega) &= -\frac{1}{(2\pi)^2} \int [f(\epsilon_s) - f(\epsilon_p)] \langle \mathbf{s}^- | e^{i\mathbf{q}\mathbf{r}} | \mathbf{p}^+ \rangle \\ &\times \langle \mathbf{p}^+ | e^{-i\mathbf{k}\mathbf{r}} | \mathbf{s}^- \rangle \delta(\omega - \epsilon_p + \epsilon_s) d\mathbf{p} d\mathbf{s}, \end{aligned} \quad (\text{D.1})$$

where $|\mathbf{p}^+\rangle$, $|\mathbf{s}^-\rangle$, and ϵ_p are the single-particles outgoing scattering states, incoming states ³¹, and the energies in the potential $V_{KS}(r)$, respectively, and f is the Fermi function. Equation (D.1) can be rewritten as

$$\begin{aligned} \text{Im } \chi_{KS}(\mathbf{q}, \mathbf{k}, \omega) &= -\frac{1}{(2\pi)^2} \int [f(\epsilon_s) - f(\epsilon_s + \omega)] \times \\ &\langle \mathbf{s}^- | e^{i\mathbf{q}\mathbf{r}} | \mathbf{p}^+ \rangle \langle \mathbf{p}^+ | e^{-i\mathbf{k}\mathbf{r}} | \mathbf{s}^- \rangle \delta(\omega - \epsilon_p + \epsilon_s) d\mathbf{p} d\mathbf{s}, \end{aligned}$$

and expanded at small ω to

$$\begin{aligned} \text{Im } \chi_{KS}(\mathbf{q}, \mathbf{k}, \omega) &= -\frac{\omega}{(2\pi)^2} \int \delta(\epsilon_p - \epsilon_F) \delta(\epsilon_s - \epsilon_F) \\ &\times \langle \mathbf{s}^- | e^{i\mathbf{q}\mathbf{r}} | \mathbf{p}^+ \rangle \langle \mathbf{p}^+ | e^{-i\mathbf{k}\mathbf{r}} | \mathbf{s}^- \rangle d\mathbf{p} d\mathbf{s}. \end{aligned} \quad (\text{D.2})$$

Now we can write by virtue of Eq. (3)

$$\begin{aligned} Q_1 &= \frac{2\pi}{v^2} \int \delta(\epsilon_p - \epsilon_F) \delta(\epsilon_s - \epsilon_F) \langle \mathbf{s}^- | [\mathbf{v} \cdot \nabla V_{KS}(\mathbf{r})] | \mathbf{p}^+ \rangle \\ &\times \langle \mathbf{p}^+ | [\mathbf{v} \cdot \nabla V_{KS}(\mathbf{r})] | \mathbf{s}^- \rangle d\mathbf{p} d\mathbf{s}, \end{aligned}$$

where the square brackets in $[\mathbf{v} \cdot \nabla V_{KS}(\mathbf{r})]$ denote that the gradient applies to $V_{KS}(\mathbf{r})$ only, leaving the wave-functions intact. We can further write

$$\begin{aligned} \langle \mathbf{s}^- | [\mathbf{v} \cdot \nabla V_{KS}(\mathbf{r})] | \mathbf{p}^+ \rangle &= \langle \mathbf{s}^- | \mathbf{v} \cdot \nabla V_{KS}(\mathbf{r}) | \mathbf{p}^+ \rangle - \langle \mathbf{s}^- | V_{KS}(\mathbf{r}) \mathbf{v} \cdot \nabla | \mathbf{p}^+ \rangle = \\ &\langle \mathbf{s} + G_0^- V_{KS} \mathbf{s}^- | \mathbf{v} \cdot \nabla V_{KS}(\mathbf{r}) | \mathbf{p}^+ \rangle - \langle \mathbf{s}^- | V_{KS}(\mathbf{r}) \mathbf{v} \cdot \nabla | \mathbf{p} + G_0^+ V_{KS} \mathbf{p}^+ \rangle, \end{aligned} \quad (\text{D.3})$$

where we have used the Lippmann-Schwinger equations ³¹

$$|\mathbf{p}^\pm\rangle = |\mathbf{p}\rangle + G_0^\pm V_{KS} |\mathbf{p}^\pm\rangle.$$

From Eq. (D.3) we have

$$\langle \mathbf{s}^- | [\mathbf{v} \cdot \nabla V_{KS}(\mathbf{r})] | \mathbf{p}^+ \rangle = i \mathbf{v} \cdot \mathbf{s} \langle \mathbf{s} | V_{KS} | \mathbf{p}^+ \rangle - i \mathbf{v} \cdot \mathbf{p} \langle \mathbf{s}^- | V_{KS} | \mathbf{p} \rangle,$$

and using formulas for the transition-matrix³¹

$$t(\mathbf{s} \leftarrow \mathbf{p}) = \langle \mathbf{s} | V_{KS} | \mathbf{p}^+ \rangle = \langle \mathbf{s}^- | V_{KS} | \mathbf{p} \rangle,$$

we have

$$\langle \mathbf{s}^- | [\mathbf{v} \cdot \nabla V_{KS}(\mathbf{r})] | \mathbf{p}^+ \rangle = i \mathbf{v} \cdot (\mathbf{s} - \mathbf{p}) t(\mathbf{s} \leftarrow \mathbf{p}),$$

and similarly

$$\langle \mathbf{p}^+ | [\mathbf{v} \cdot \nabla V_{KS}(\mathbf{r})] | \mathbf{s}^- \rangle = -i \mathbf{v} \cdot (\mathbf{s} - \mathbf{p}) t^*(\mathbf{s} \leftarrow \mathbf{p}).$$

We can then write for the noninteracting-electrons part of the friction coefficient

$$Q_1 = \frac{2\pi}{v^2} \int \delta(\epsilon_p - \epsilon_F) \delta(\epsilon_s - \epsilon_F) [\mathbf{v} \cdot (\mathbf{s} - \mathbf{p})]^2 |t(\mathbf{s} \leftarrow \mathbf{p})|^2 d\mathbf{p} ds. \quad (\text{D.4})$$

Recalling the expression of the differential cross-section through the T -matrix element³¹

$$\frac{d\sigma(\theta_{\mathbf{s}\hat{\mathbf{p}}})}{d\Omega_{\mathbf{s}\hat{\mathbf{p}}}} = (2\pi)^4 |t(\mathbf{s} \leftarrow \mathbf{p})|^2$$

and performing some integrations in Eq. (D.4) explicitly, we arrive at Eq. (1).

Appendix E. A proof that for a finite system the tensorial sum rules of Eqs. (30)-(32) lead to the scalar sum rule of Eq. (13)

Equation (32) can be rewritten as

$$\frac{c}{\omega^2} \int \hat{\chi}_{ik}(\mathbf{r}, \mathbf{r}', \omega) \nabla'_k \nabla'_j V_0(\mathbf{r}') d\mathbf{r}' = c \int \hat{\chi}_{ik}(\mathbf{r}, \mathbf{r}', \omega) \nabla'_k r'_j d\mathbf{r}' - n_0(\mathbf{r}) \delta_{ij}. \quad (\text{E.1})$$

The next step, which involves integration by parts, requires the response function to vanish at infinity and, therefore, it applies to bounded systems only. For the latter case we can write multiplying Eq. (E.1) scalarly from the left by ∇ and using Eq. (16)

$$\int \chi(\mathbf{r}, \mathbf{r}', \omega) [\nabla'_j V_0(\mathbf{r}') - \omega^2 r'_j] d\mathbf{r}' = \nabla_j n_0(\mathbf{r}),$$

and after inverting

$$\int \chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) \nabla_j n_0(\mathbf{r}') d\mathbf{r}' = \nabla_j V_0(\mathbf{r}) - \omega^2 r_j. \quad (\text{E.2})$$

A similar relation holds for χ_{KS}

$$\int \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r}', \omega) \nabla_j n_0(\mathbf{r}') d\mathbf{r}' = \nabla_j V_{KS}(\mathbf{r}) - \omega^2 r_j. \quad (\text{E.3})$$

Subtracting Eq. (E.2) from Eq. (E.3) and using the definition of Eq. (15), we immediately arrive at Eq. (13) [compare with Ref. 15].

Appendix F. Explicit expressions for the KS current-density response function, the xc kernel, and the \mathbf{x} vector of Eq. (22) for a system with spherical symmetry

F.1. KS current-density response function

The KS response function can be explicitly written as

$$\begin{aligned} \hat{\chi}_{KS,ij}(\mathbf{r}, \mathbf{r}', \omega) &= \frac{1}{c} n_0(r) \delta(\mathbf{r} - \mathbf{r}') \delta_{ij} - \frac{1}{4c} \times \\ &\sum_{\alpha\beta} \frac{f_\alpha - f_\beta}{\omega - \epsilon_\beta + \epsilon_\alpha + i\eta} [\psi_\alpha^*(\mathbf{r}) \nabla_i \psi_\beta(\mathbf{r}) - \psi_\beta(\mathbf{r}) \nabla_i \psi_\alpha^*(\mathbf{r})] \\ &\times [\psi_\beta^*(\mathbf{r}') \nabla'_j \psi_\alpha(\mathbf{r}') - \psi_\alpha(\mathbf{r}') \nabla'_j \psi_\beta^*(\mathbf{r}')] , \end{aligned} \quad (\text{F.1})$$

where $\psi_\alpha(\mathbf{r})$ and ϵ_α are the single-particle wave-function and eigenenergy, respectively, in the state α , and f_α is the occupation number of this state. From the spherical symmetry of the problem it is easy to conclude that both $\hat{\chi}_{KS}$ and \hat{f}_{xc} leave invariant the subspace of the vectors of the form

$$a(r) \mathbf{v} + b(r) (\mathbf{r} \cdot \mathbf{v}) \mathbf{r},$$

where $a(r)$ and $b(r)$ are arbitrary scalar functions of $r = |\mathbf{r}|$, and, hence, both \mathbf{x} and the solution \mathbf{y} of Eq. (24) are the vectors from the same subspace. Furthermore, by the definition (23), \mathbf{y} is the transverse vector, which property imposes the fulfillment of the relation

$$a'(r) + 4r b(r) + r^2 b'(r) = 0,$$

and, therefore, Eq. (24) effectively becomes an equation with respect to one unknown scalar function of the radial coordinate. With use of Eq. (F.1), we arrive at the equalities which are sufficient to evaluate $\chi_{\hat{KS}}$ -dependent quantities in Eq. (24)

$$c \int \hat{\chi}_{KS,ij}(\mathbf{r}, \mathbf{r}', \omega) a(r', \omega) \delta_{jk} d\mathbf{r}' = \tilde{a}(r, \omega) \delta_{ik} + \tilde{b}(r, \omega) r_i r_k, \quad (\text{F.2})$$

$$c \int \hat{\chi}_{KS,ij}(\mathbf{r}, \mathbf{r}', \omega) \nabla'_j \nabla'_k F(r') d\mathbf{r}' = k(r, \omega) \delta_{ik} + m(r, \omega) r_i r_k, \quad (\text{F.3})$$

where

$$\tilde{a}(r) = n_0(r) a(r) + q(r),$$

$$\tilde{b}(r, \omega) = -q(r)/r^2 + p(r)/r^4,$$

and

$$q(r) = -\frac{n_0(r)}{r} \int_0^r a(r') dr' - \frac{\omega}{4\pi r^3} \sum_{\alpha, l_\beta} f_\alpha (\delta_{l_\alpha-1, l_\beta} l_\alpha^2 - \delta_{l_\alpha, l_\beta-1} l_\beta^2) y_\alpha(r)$$

$$\begin{aligned}
 & \times \int_0^\infty dr' \left[G_{l_\beta, \epsilon_\alpha + \omega}(r, r') - G_{l_\beta, \epsilon_\alpha - \omega}^*(r, r') \right] y_\alpha(r') \int_\infty^{r'} a(r'') dr'' \\
 & + \frac{1}{4\pi r^3} \sum_{\alpha, l_\beta} f_\alpha (\delta_{l_\alpha - 1, l_\beta} l_\alpha^3 + \delta_{l_\alpha, l_\beta - 1} l_\beta^3) y_\alpha(r) \int_0^\infty dr' \left[G_{l_\beta, \epsilon_\alpha + \omega}(r, r') + G_{l_\beta, \epsilon_\alpha - \omega}^*(r, r') \right] \frac{y_\alpha(r')}{r'} \\
 & \times \left[a(r') - \frac{1}{r'} \int_\infty^{r'} a(r'') dr'' \right], \tag{F.4}
 \end{aligned}$$

$$\begin{aligned}
 p'(r) &= 2rq(r) - r^2[a(r)n_0(r)]' + \frac{\omega}{2\pi} \sum_{\alpha, l_\beta} f_\alpha (\delta_{l_\alpha - 1, l_\beta} l_\alpha^2 - \delta_{l_\alpha, l_\beta - 1} l_\beta^2) y_\alpha(r) \\
 & \times \int_0^\infty dr' \left[G_{l_\beta, \epsilon_\alpha + \omega}(r, r') - G_{l_\beta, \epsilon_\alpha - \omega}^*(r, r') \right] \frac{y_\alpha(r')}{r'} \left[a(r') - \frac{1}{r'} \int_\infty^{r'} a(r'') dr'' \right] - \frac{\omega^2}{2\pi} \sum_{\alpha, l_\beta} f_\alpha \\
 & \times (\delta_{l_\alpha - 1, l_\beta} l_\alpha + \delta_{l_\alpha, l_\beta - 1} l_\beta) y_\alpha(r) \int_0^\infty dr' \left[G_{l_\beta, \epsilon_\alpha + \omega}(r, r') + G_{l_\beta, \epsilon_\alpha - \omega}^*(r, r') \right] y_\alpha(r') \int_\infty^{r'} a(r'') dr'', \tag{F.5}
 \end{aligned}$$

$$\begin{aligned}
 k(r) &= -\frac{\omega}{4\pi r^3} \sum_{\alpha, l_\beta} f_\alpha (l_\alpha^2 \delta_{l_\beta, l_\alpha - 1} - l_\beta^2 \delta_{l_\alpha, l_\beta - 1}) y_{l_\alpha, k_\alpha}(r) \int_0^\infty \left[G_{l_\beta, \epsilon_\alpha + \omega}(r, r') - G_{l_\beta, \epsilon_\alpha - \omega}^*(r, r') \right] y_{l_\alpha, k_\alpha}(r') F'(r') dr', \\
 \frac{[r^4 m(r)]'}{r^2} &= -k'(r) - \frac{\omega^2}{2\pi r^2} \sum_{l_\beta, \alpha} f_\alpha (l_\alpha \delta_{l_\beta, l_\alpha - 1} + l_\beta \delta_{l_\alpha, l_\beta - 1}) y_{l_\alpha, k_\alpha}(r) \\
 & \times \int_0^\infty [G_{l_\beta, \epsilon_\alpha + \omega}(r, r') + G_{l_\beta, \epsilon_\alpha - \omega}^*(r, r')] y_{l_\alpha, k_\alpha}(r') F'(r') dr', \tag{F.6}
 \end{aligned}$$

where $y_\alpha(r)$ are the solutions of the radial Schrödinger equation

$$\left[\frac{d^2}{dr^2} - \frac{l_\alpha(l_\alpha + 1)}{r^2} - 2V_{KS}(r) + 2\epsilon_\alpha \right] y_\alpha(r) = 0,$$

and

$$G_{l, \epsilon}(r, r') = \sum_{k_\beta} \frac{y_{l, k_\beta}(r) y_{l, k_\beta}(r')}{\epsilon + i\eta - \epsilon_\beta}$$

is the Green's function.

F.2. Exchange and correlation kernel

In the case of spherical symmetry, we can write

$$\int \hat{f}_{xc, ij}(\mathbf{r}, \mathbf{r}', \omega) [a(r', \omega) \delta_{jk} + b(r', \omega) r'_j r'_k] d\mathbf{r}' = \tilde{a}(r, \omega) \delta_{ik} + \tilde{b}(r, \omega) r_i r_k, \tag{F.7}$$

and, with use of the equations of Sec. 3.1, we have

$$\begin{aligned}
\tilde{a}(r) &= \frac{ic}{3r\omega^2 n_0(r)} \left\{ 3 \left[4irb(r)\epsilon_{xc}(r)n_0(r) + i\epsilon_{xc}(r)n_0(r)(a'(r) + r^2b'(r)) + r\omega\tilde{\eta}'_{xc}(r)(rb_1(r) + a'_1(r)) \right] \right. \\
&\quad \left. + 3\omega\tilde{\zeta}_{xc}(r)[4rb_1(r) + a'_1(r) + r^2b'_1(r)] + \omega\tilde{\eta}_{xc}(r)[7a'_1(r) + r(10b_1(r) + rb'_1(r) + 3a''_1(r))] \right\} \\
\tilde{b}(r) &= \frac{ic}{3r^3\omega^2 n_0(r)} \left\{ 12ir^2b(r)n_0(r)\epsilon'_{xc}(r) + 3ir n_0(r)a'(r)\epsilon'_{xc}(r) + 3ir^3n_0(r)b'(r)\epsilon'_{xc}(r) \right. \\
&\quad + 12r^2\omega b_1(r)\tilde{\zeta}'_{xc}(r) + r^2\omega b_1(r)\tilde{\eta}'_{xc}(r) - 3\omega\tilde{\zeta}_{xc}(r)a'_1(r) - \omega\tilde{\eta}_{xc}(r)a'_1(r) + 3r\omega\tilde{\zeta}'_{xc}(r)a'_1(r) \\
&\quad + r\omega\tilde{\eta}'_{xc}(r)a'_1(r) + 15r^2\omega\tilde{\zeta}_{xc}(r)b'_1(r) + 23r^2\omega\tilde{\eta}_{xc}(r)b'_1(r) + 3r^3\omega\tilde{\zeta}'_{xc}(r)b'_1(r) + 4r^3\omega\tilde{\eta}'_{xc}(r)b'_1(r) \\
&\quad - 3i\epsilon_{xc}(r)n_0(r)[a'(r) - r(5rb'(r) + a''(r) + r^2b''(r))] + 3r\omega\tilde{\zeta}_{xc}(r)a''_1(r) + r\omega\tilde{\eta}_{xc}(r)a''_1(r) \\
&\quad \left. + r^3\omega[3\tilde{\zeta}_{xc}(r) + 4\tilde{\eta}_{xc}(r)]b''_1(r) \right\}, \tag{F.8}
\end{aligned}$$

where $a_1(r) = a(r)/n_0(r)$ and $b_1(r) = b(r)/n_0(r)$.

We are using the LDA to the tensorial xc kernel of Sec. 3.1, with the low-frequency expansion of $f_{xc,L}^h(n, \omega)$ and $f_{xc,T}^h(n, \omega)$ up to the first order in ω . Using the equalities ²¹

$$\begin{aligned}
f_{xc,L}^h(n, 0) - \frac{4}{3}f_{xc,T}^h(n, 0) - \epsilon''_{xc}(n) &= 0, \\
\frac{\partial f_{xc,L}^h(n, \omega)}{\partial \omega} \Big|_{\omega=0} - \frac{4}{3} \frac{\partial f_{xc,T}^h(n, \omega)}{\partial \omega} \Big|_{\omega=0} &= 0,
\end{aligned}$$

we have from Eqs. (29)

$$\begin{aligned}
\tilde{\zeta}_{xc}(n, \omega) &= 0, \\
\tilde{\eta}_{xc}(n, \omega) &= \frac{in^2}{\omega} \left[f_{xc,T}^h(n, 0) + i\omega \frac{\partial \text{Im} f_{xc,T}^h(n, \omega)}{\partial \omega} \Big|_{\omega=0} \right]. \tag{F.9}
\end{aligned}$$

For $f_{xc,T}^h(n, 0)$, we take use of its expression through the shear modulus μ_{xc}

$$f_{xc,T}^h(n, 0) = \frac{\mu_{xc}(n)}{n^2}.$$

For the local density such that $1 \leq r_s \leq 5$ we obtain $\mu_{xc}(n)$ by the interpolation between the values of Ref. ²¹. For $r_s < 1$, we use the high-density approximation ³²

$$\mu_{xc}(n) = \frac{nk_F(n)}{10\pi}.$$

For $\frac{\partial f_{xc,T}^h(n, \omega)}{\partial \omega} \Big|_{\omega=0}$, we are using Eq. (15) of Ref. ²¹.

F.3. The \mathbf{x} vector of Eq. (22)

Using the definition of Eq. (22) together with Eq. (33) we can write

$$\mathbf{x}(\omega) = (n_0 - \bar{n}_0)\mathbf{v} + \frac{c}{\omega^2} \hat{\chi}_{KS}(\omega) \nabla \chi_{KS}^{-1}(\omega) \nabla(n_0 \mathbf{v}),$$

where we have explicitly written the frequency dependence of the functions. Expanding to the first order in ω

$$\chi_{KS}^{-1}(\omega) \nabla(n_0 \mathbf{v}) = \chi_{KS}^{-1}(0) \nabla(n_0 \mathbf{v}) + \omega \left. \frac{\partial \chi_{KS}^{-1}(\omega)}{\partial \omega} \right|_{\omega=0} \nabla(n_0 \mathbf{v})$$

and using the static sum rule (C.1), we can write

$$\begin{aligned} \mathbf{x}(\omega) &= (n_0 - \bar{n}_0)\mathbf{v} + \frac{c}{\omega^2} \hat{\chi}_{KS}(\omega) \nabla(\mathbf{v} \cdot \nabla V_{KS}) \\ &\quad - \frac{c}{\omega} \hat{\chi}_{KS}(\omega) \nabla \chi_{KS}^{-1}(0) \left[\frac{\partial \chi_{KS}(\omega)}{\partial \omega} \right]_{\omega=0} (\mathbf{v} \cdot \nabla V_{KS}). \end{aligned} \quad (\text{F.10})$$

It must be noted that an expansion in ω of $\hat{\chi}_{KS}(\omega)$ applied to a gradient of an ω -independent function starts from the ω^2 term and, therefore, the second and the third terms in the above expression have leading terms of ω^0 and ω^1 , respectively. To evaluate Eq. (F.10) to the first order in ω we derive and use the following equalities:

$$\frac{c}{\omega^2} \hat{\chi}_{KS}(\omega) \nabla(\mathbf{v} \cdot \nabla V_{KS}) = a(r, \omega) \mathbf{v} + b(r, \omega) (\mathbf{v} \cdot \mathbf{r}) \mathbf{r}, \quad (\text{F.11})$$

$$\begin{aligned} a(r, \omega) &= \frac{9h(r, \omega) - 15g(r, \omega)}{16\pi} - n_0(r), \\ b(r, \omega) &= \frac{45g(r, \omega) - 15h(r, \omega)}{16\pi r^2}, \end{aligned} \quad (\text{F.12})$$

$$\begin{bmatrix} h(r, \omega) \\ g(r, \omega) \end{bmatrix} = \begin{bmatrix} h_0(r) \\ g_0(r) \end{bmatrix} + \omega \begin{bmatrix} h_1(r) \\ g_1(r) \end{bmatrix} + \dots, \quad (\text{F.13})$$

$$\begin{bmatrix} h_0(r) \\ g_0(r) \end{bmatrix} = \frac{2R}{\pi r^3} \sum_{l=0}^{\infty} \begin{bmatrix} H_l(k_F, k_F, r) \\ G_l(k_F, k_F, r) \end{bmatrix} \cos[\delta_{l-1}(k_F) - \delta_l(k_F)], \quad (\text{F.14})$$

$$\begin{aligned} \begin{bmatrix} h_1(r) \\ g_1(r) \end{bmatrix} &= \frac{R}{\pi k_F r^3} \sum_{l=0}^{\infty} \begin{bmatrix} H_l(k_F, k_F, r) \\ G_l(k_F, k_F, r) \end{bmatrix} \left\{ \cos[\delta_{l-1}(k_F) - \delta_l(k_F)] [\delta'_{l-1}(k_F) + \delta'_l(k_F)] - \right. \\ &\quad \left. \frac{2l}{k_F} \sin[\delta_{l-1}(k_F) - \delta_l(k_F)] \right\} + \left\{ \left(\frac{\partial}{\partial k_\beta} - \frac{\partial}{\partial k_\alpha} \right) \begin{bmatrix} H_l(k_\alpha, k_\beta, r) \\ G_l(k_\alpha, k_\beta, r) \end{bmatrix} \right\}_{k_\alpha=k_\beta=k_F} \\ &\quad \times \sin[\delta_{l-1}(k_F) - \delta_l(k_F)], \end{aligned} \quad (\text{F.15})$$

$$\begin{aligned} \begin{bmatrix} H_l(k_\alpha, k_\beta, r) \\ G_l(k_\alpha, k_\beta, r) \end{bmatrix} &= \begin{bmatrix} 2/3 \\ 2/15 \end{bmatrix} l^2 y_{l,k_\alpha}(r) y_{l-1,k_\beta}(r) \\ &+ \begin{bmatrix} 1/3 \\ 1/5 \end{bmatrix} l r [y_{l-1,k_\beta}(r) y'_{l,k_\alpha}(r) - y_{l,k_\alpha}(r) y'_{l-1,k_\beta}(r)]. \quad (\text{F.16}) \end{aligned}$$

Equations (F.11) - (F.16) are enough to explicitly evaluate the second term and to apply the first operator from the right in the third term of Eq. (F.10). We, however, did not find a way to explicitly apply $\chi_{KS}^{-1}(0)$ in the third term and, therefore, we invert $\chi_{KS}(0)$ on the set of the basis functions of Eq. (34) and finally use Eqs. (F.3) and (F.6).

Acknowledgements

G. V. and Y. T. acknowledge, respectively, financial support by the Department of Energy grant DE-FG02-05ER46203 and a Grant-in-Aid for Scientific Research in Priority Areas (No.17064004) of MEXT, Japan.

1. J. R. Sabin and E. Brändas (eds.), *Theory of the interaction of swift ions with matter*, Advances in Quantum Chemistry, Vol. 45 (Elsevier Academic Press, 2004).
2. P. M. Echenique, F. Flores and R. H. Ritchie, *Solid State Physics* **43**, p. 229 (1990).
3. P. M. Echenique, R. M. Nieminen and R. H. Ritchie, *Solid State Commun.* **37**, p. 779 (1981).
4. P. M. Echenique, R. M. Nieminen, J. C. Ashley and R. H. Ritchie, *Phys. Rev. A* **33**, p. 897 (1986).
5. V. U. Nazarov, J. M. Pitarke, C. S. Kim and Y. Takada, *J. Phys.: Condens. Matter* **16**, p. 8621 (2004).
6. J. Finneman, PhD thesis, Aarhus University, (the Institute of Physics, 1968). unpublished.
7. W. Kohn and L. J. Sham, *Phys. Rev.* **140**, p. A1133 (1965).
8. I. Nagy, A. Arnau and P. M. Echenique, *Phys. Rev. A* **40**, p. 987 (1989).
9. Y. S. Sayasov and N. R. Tahir, *Europhys. Lett.* **23**, p. 641 (1993).
10. V. U. Nazarov, J. M. Pitarke, C. S. Kim and Y. Takada, *Phys. Rev. B* **71**, p. 121106(R) (2005).
11. E. K. U. Gross and W. Kohn, *Phys. Rev. Lett.* **55**, 2850(Dec 1985).
12. K. Huang, *Proc. Phys. Soc. London* **60**, p. 161 (1948).
13. O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B* **13**, p. 4274 (1976).
14. J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, p. 5048 (1981).
15. G. Vignale, *Phys. Lett. A* **209**, p. 206 (1995).
16. G. Vignale and W. Kohn, *Phys. Rev. Lett.* **77**, p. 2037 (1996).
17. G. Vignale, C. A. Ullrich and S. Conti, *Phys. Rev. Lett.* **79**, p. 4878 (1997).
18. C. A. Ullrich and G. Vignale, *Phys. Rev. B* **65**, p. 245102 (2002).
19. N. Sai, M. Zwolak, G. Vignale and M. Di Ventra, *Phys. Rev. Lett.* **94**, p. 186810 (2005).
20. V. U. Nazarov, J. M. Pitarke, Y. Takada, G. Vignale and Y.-C. Chang, *Phys. Rev. B* **76**, p. 205103 (2007).
21. Z. Qian and G. Vignale, *Phys. Rev. B* **65**, p. 235121 (2002).
22. G. Vignale and W. Kohn, Current-density functional theory of time-dependent linear response: the local density approximation, in *Electronic Density Functional The-*

- ory: *Recent Progress and New Directions*, eds. J. Dobson, M. P. Das and G. Vignale (Plenum Press, New York, 1998).
23. H. Winter, J. I. Juaristi, I. Nagy, A. Arnau and P. M. Echenique, *Phys. Rev. B* **67**, p. 245401 (2003).
 24. J. Bøttiger and F. Bason, *Radiat. Effects* **2**, p. 105 (1969).
 25. J. H. Ormrod and H. E. Duckworth, *Can. J. Phys.* **41**, p. 1424 (1963), J. H. Ormrod, J. R. Macdonald, and H. E. Duckworth, *ibid.* **43**, 275 (1965).
 26. D. Ward *et al.*, *Can. J. Phys.* **57**, p. 645 (1979).
 27. G. Högberg, *Phys. Status Solidi B* **46**, p. 829 (1971).
 28. R. Vincent and I. Nagy, *Nucl. Instr. Meth. B* **256**, p. 182 (2007).
 29. M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger and J. G. Snijders, *Phys. Rev. Lett.* **88**, p. 186401 (2002).
 30. M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger and J. G. Snijders, *J. Chem. Phys.* **118**, p. 1044 (2003).
 31. J. R. Taylor, *Scattering theory* (John Wiley & Sons, New York, 1972).
 32. S. Conti and G. Vignale, *Phys. Rev. B* **60**, p. 7966 (1999).